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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

High Polymer Compositions having High Light Transmission and Toughness

We, AMERICAN CYANAMID COMPANY, a corporation organised under the Laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to transparent, moldable resinous compositions. More particularly, this invention relates to novel thermoplastic molding compositions characterized by their high impact strength, transparency, toughness, rigidity and weatherability.

It is known that various rubbery materials may be mechanically admixed or incorporated into thermoplastic polymers to obtain compositions which may be readily molded, by a variety of techniques, to form very tough plastic compositions suitable for many purposes. One drawback in the compositions produced in this manner has been that products produced from these compositions, and the compositions per se, are opaque or cloudy masses and therefore are not useful for many purposes to which they are otherwise well suited. Additionally, many of these prior art compositions are rather poor in regard to their rigidity, impact strength and weatherability.

We have now discovered that tough, transparent, molding compositions having high impact strength, rigidity and weatherability can be produced by either physically blending a glassy polymer with a rubber which has been grafted to adjust its refractive index to within 0.009 of that of the glassy polymer or physically blending a grafted rubber with a glassy polymer which has been produced so as to have a refractive index within 0.009 of the existing grafted rubber.

[Price 4s. 6d.]

Previous to our invention, transparent thermoplastic molding compositions were produced in a variety of ways, each presenting its own specific deficiency in regard to the method of production or the compound produced. In U.S. Patent 2,941,977, transparent compositions are produced; however, the constituents thereof are limited to copolymers of an alkenyl aromatic compound and butadiene-styrene rubbers. Additionally only a tolerance of 0.004 in the matching of the refractive indices of both constituents is possible. In U.S. Patent 3,029,223 the ingredients of the molding composition are limited to butadiene-styrene copolymers and styrene and methyl methacrylate monomers. The compositions must be produced by interpolymerizing all of the ingredients simultaneously at elevated temperatures. Because of viscosity restrictions, this process limits the quantity of rubber that can be used and incorporated into the final product. The resultant compositions have relatively low impact strengths because of this limitation.

The process, and compositions produced thereby, of the present invention are superior in many respects to those of the above-enumerated prior art. Thus no complex interpolymerization of the ingredients is necessary. Physical blending of the components is all that is necessary. Further, a greater variety of rubbery components and polymeric components may be utilized, thereby enabling a more complete control of the properties of the final molding compositions. The quantity of rubber that can be incorporated into the final products is greater than that possible hitherto, and therefore materially increased impact strengths can be obtained. Again, the compositions in general, have impact strengths higher than commercially available compositions and, a greater latitude than heretofore

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known in matching the refractive indices of the components is tolerable, thereby enabling the use of a greater quantity of any specific compound in each of the components.

Our novel process, whereby our novel molding compositions are produced, comprises either of two analogous procedures depending upon the starting material involved. The processes involve physically blending a glassy polymeric resin and a grafted rubber, either constituent having been modified in such a manner so as to conform its refractive index to within 0.009 of that of the other constituent with which it is to be blended. When the refractive index of the glassy polymer is known, the rubber is modified by grafting monomers onto it so as to conform its refractive index to within 0.009 of that of the polymer. When the refractive index of the grafted rubber is known, the glassy polymer is produced by calculating the amount of specific monomers needed to produce a polymer with a refractive index within 0.009 of that of the grafted rubber and polymerizing said monomers. In each instance, the two components are then physically admixed with each other to produce our novel transparent, molding compositions.

We have unexpectedly found that when grafting a rubber with a certain ratio of monomer or monomers the refractive index of the rubber-graft system assumes a new refractive index. The extent of this change depends upon the amount and type of monomers involved. If the combined monomers, as polymer, have a refractive index lower than that of the rubber, the refractive index of the rubber-graft system will be lower than the unmodified rubber; conversely, if the monomers, as polymer, have a higher refractive index than the rubber the refractive index of this rubber-graft system will be greater. This new refractive index species retains its identity after mechanical blending with the resin portion.

The first step in the actual procedure of our novel process, when the refractive index of the grafted rubber is already known, is to estimate the amount of monomers necessary to produce a polymer having a refractive index within 0.009 of that of the grafted rubber. This estimation for the polymeric component can be carried out and obtained from a modified Eisenlohr equation relating mole fraction, refractive index and polymer composition. This modified equation is as follows:

$$n = \frac{\sum_{i=1}^K (N_i M_i n_i)}{\sum_{i=1}^K (N_i M_i)}$$

wherein N_i is the mole fraction of monomer i , M_i is the molecular weight of monomer i , n_i is the refractive index of the homopolymer of the monomer i , wherein i runs from 1 to K , wherein K is the number of monomers involved in the polymerization, and n is the refractive index of the grafted rubber with which the polymer is to be admixed. (Throughout this specification, n in the modified Eisenlohr equation is the refractive index of a homopolymer of the monomer i which has been polymerized to a degree above that at which the refractive index is dependent upon the molecular weight of the homopolymer.)

By studying the equation, it can be seen that the molar amount of monomers necessary to produce a polymer having a certain refractive index can be calculated. Depending upon the number of monomers employed, K , in the polymerization, the molar amounts of monomers will vary with each system. That is to say, when one monomer is used, e.g. a methacrylic acid ester, the equation need not be employed because the homopolymer will always have the same refractive index. However, when another monomer is added, a calculation must be made to determine the molar amounts of each monomer necessary to produce a copolymer which would have a refractive index within 0.009 of the known refractive index of the grafted rubber.

By utilizing the above equation, the refractive index of a polymer capable of being produced from the polymerizable monomers can be calculated and by varying the mole fraction of any of the monomers, we can vary the refractive index of the polymer so that it coincides within 0.009 of that of the grafted rubber with which the polymer is to be blended. By making such a calculation and subsequently blending the derived amounts of the produced constituent with that already existing, i.e. the grafted rubber, our novel transparent molding compositions can be produced.

Utilizing the information gained from the above-enumerated equation, the next step whereby our novel molding compositions are produced, comprises polymerizing the monomeric material (or mixture of monomeric materials) to produce a homopolymer (or copolymer) which constitutes component (1), of the novel compositions of the present invention. The polymerization can be carried out utilizing any known polymerization procedure. A method which may be used for example, comprises conducting the polymerization in the presence of a free-radical generating catalyst and a polymerization regulator, at temperatures of from 10°C. to 90°C. Any known free-radical generating catalyst which initiates the polymerization of, for example, monomeric methyl methacrylate, may be used. Suitable catalysts include, for example, the organic peroxides such as methyl ethyl ketone

peroxide, benzoyl peroxide; the hydroperoxides such as cumene hydroperoxide; the persulfate type compounds such as potassium persulfate, or catalysts such as azobisisobutyronitrile. Additional examples of such catalysts are lauroyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy) hexane, the dialkyl peroxides, e.g., diethyl peroxide, dipropyl peroxide, dilauryl peroxide, dioleoyl peroxide, distearyl peroxide, di-(tertiary-butyl) peroxide and di-(tertiary-amyl) peroxide, such peroxides often being designated as ethyl, propyl, lauryl, oleyl, stearyl, tertiary-butyl and tertiary-amyl peroxides; the alkyl hydrogen peroxides, e.g., tertiary-butyl hydrogen peroxide (tertiary-butyl hydroperoxide), tertiary-amyl hydrogen peroxide (tertiary-amyl hydroperoxide); symmetrical diacyl peroxides, for instance, peroxides which commonly are known under such names as acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl peroxide, malonyl peroxide, succinyl peroxide, phthaloyl peroxide, benzoyl peroxide; fatty oil acid peroxides, e.g., coconut oil acid peroxides; unsymmetrical or mixed diacyl peroxides, e.g., acetyl benzoyl peroxide, propionyl benzoyl peroxide; terpene oxides, e.g. ascaridole; and salts of inorganic per-acids, e.g. ammonium persulfate, sodium persulfate, sodium percarbonate, potassium percarbonate, sodium perborate, potassium perborate, sodium perphosphate, and potassium perphosphate. Other examples of organic peroxide catalysts which may be employed are the following; tetralin hydroperoxide, tertiary-butyl diperphthalate, tertiary-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide, urea peroxide, caprylyl peroxide, p-chlorobenzoyl peroxide, 2,2-bis(tertiary-butylperoxy) butane, hydroxyphenyl peroxide and the diperoxide of benzaldehyde. Generally the water-soluble, as well as the monomer-soluble, types of catalyst may be employed in amounts ranging from 0.05 to 5.0 parts, by weight, of the monomer employed.

When emulsion polymerization processes are employed, any available emulsifier may be used, for example compounds such as fatty acid soaps, rosin soaps, sodium lauryl sulfate, non-ionic emulsifiers such as polyethoxy alkylated phenols, compounds such as dioctyl sodium sulfosuccinate, dihexyl sodium sulfosuccinate and the like, in amounts ranging from 1% to 8%, by weight, preferably 4% to 5%, by weight, based on the amount of the monomers employed.

Polymerization regulators may be used in any of these processes, with compounds such as the organic sulphur compounds, i.e. the thio acids, mercaptans such as benzyl mercaptan, aliphatic mercaptans possessing at least 6 carbon atoms such as octyl, dodecyl and tertiary dodecyl mercaptan, mixtures of mercaptans; nitrohydrazine, amino compounds and carbon tetrachloride being exemplary. It is preferred however, to use the alkyl mer-

captans of low water solubility, such as dodecyl mercaptan, in amounts ranging from 0.01% to 5.0% by weight, of the monomers employed.

There may also be added to the polymers, after the polymerization, such ingredients as light stabilizers, heat stabilizers, antioxidants, lubricants, plasticizers, pigments, fillers and dyes, without detracting from the unique properties of our novel molding compositions.

The refractive index estimation for the grafted rubber component is somewhat more complex than for the polymer component. Here the refractive index is not defined by the equation relating mole fraction, refractive index and polymer composition. It involves a refractive index composite that cannot be estimated via an arithmetic average of the two components: the rubber and the polymer formed in the grafting step. The procedure is as follows: The refractive index of several diverse monomer compositions (the monomers remain the same only their relative quantities the changed) for grafting, as polymer, is calculated using the above modified Eisenlohr equation. These refractive index values are plotted against the refractive index of their respective grafted rubbers. Figure 1 shows the graphic plots of the refractive indices of several styrene-acrylonitrile-methyl methacrylate ter-polymers and their corresponding grafted rubbers. Figure 2 is a plot of various refractive indices of styrene-methyl methacrylate-acrylonitrile terpolymers. In this Figure, PMMA stands for polymethyl methacrylate and PAN stands for polyacrylonitrile. From Figure 1 and Figure 2 one can estimate, for any other possible grafted rubber refractive for grafting to achieve it. This procedure must be repeated anew if any of the following are changed in the graft system: types and number of monomers, types of rubber or the rubber-monomer ratio.

Using Figures 1 and 2, the following example clearly illustrates the procedure for determining a grafted rubber composition to match a previously prepared transparent terpolymer with a refractive index of, say, 1.523. From Figure 1, the refractive index of the grafted rubber necessary i.e. about 1.523, is read from the ordinate of the graph. The point representing this index is then traced to the connecting plotted line and then downwardly to the abscissa. The approximate refractive index value for the polymer of the monomers to be grafted is then obtained. It can be seen that the polymer should have a refractive index of about 1.534. This value is then used by referring to Figure 2 from which the various monomer compositions available for grafting to achieve the desired graft rubber refractive index may be found. That is, any compositional point along the 1.535 line in Figure 2 or about 0.009 on either side thereof can be used. Any of these terpolymer

compositions then will produce a grafted rubber of a refractive index of about 1.523 when grafted, as monomers, on the rubber backbone.

5 The only limitation which must be placed on the components, i.e. the polymer and the grafted rubber employed, before a transparent molding composition containing them can be produced by blending said components, is that the polymer and the grafted rubber must themselves be transparent. That is to say, if a transparent molding composition is to be produced, the monomer or monomers to be polymerized to the glassy polymer must be capable of producing a transparent polymer themselves and conversely, a transparent grafted rubber must be able to be produced from the rubber and monomer chosen to be grafted thereon. In order to ascertain whether a specific polymer will be transparent, one need only consult the prior art to determine if such a polymer can be produced from the monomers contemplated. Therefore, to determine whether transparent homopolymers, copolymers, terpolymers, etc. of, e.g. methacrylic acid esters, can be prepared with various copolymerizable monomers, one need only consult the disclosure set forth in, for example, U.S. Patents 2,836,580, 2,854,439, 2,829,125, 2,829,128, 3,009,895, or other patents constituting the prior art. If transparent polymers cannot be produced from the monomeric material or materials, the monomers contemplated cannot be used in our process. In regard to the grafted rubbers, if the monomers being grafted thereon in the same concentration will result in transparent polymers upon polymerization, the grafted rubbers themselves will also be transparent.

40 It can be seen, therefore, that the only criteria which need be followed in the use of either component of our invention is that the components utilized have refractive indices within 0.009 of each other and that each component is clear and transparent.

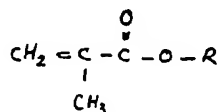
45 The grafted rubbers employed as component (2) in our novel molding compositions are prepared by any known polymerization process, and preferably any of the methods disclosed above in regard to the polymer production system may be used. When emulsifiers are employed in the graft polymerization, they should be added, in amounts below the critical micelle concentration. If amounts greater than this are employed, polymer is formed outside of the vicinity of the rubber latex particles present in the polymerization medium. The critical micelle concentration in each instance may be determined by a soap titration. An additional method for producing the grafted rubbers which may be employed is disclosed, for example, in U.S. Patent No. 2,755,270.

65 Any polymeric rubbery materials may be used to form the backbone of the second com-

ponent of our novel compositions, with such rubbers as polybutadienes, poly (methyl methacrylate/butadiene), poly(styrene/butadienes), natural or synthetic polyisoprene, polyisobutylene, poly(isobutylene/isoprene) copolymers, the Buna N-type rubbers which are the poly(acrylonitrile/butadienes), polyalkylacrylates, polymers and copolymers which are rubbery, polyurethane, rubber poly(alkylenes), i.e. poly(ethylene-propylene) copolymer rubber 75 being exemplary.

The rubbery backbone materials, mentioned above, are grafted, in our novel process, with from 10% to 100%, preferably 20% to 100%, by weight, of monomer, based on the weight of the rubber, that is to say, the above amounts are those which generally will be used to produce the grafted rubbers, depending, of course, on the refractive index of the glassy polymer with which it is to be subsequently blended. 85

The polymers used to form the glassy polymer, i.e. component (1) may be produced from any polymerizable monomer; however the preferred monomers are the methacrylic acid 90 esters having the formula



(I)

wherein R represents an alkyl radical containing from 1 to 6 carbon atoms, inclusive. Compounds which are represented by the above formula and consequently may be used in the present invention include methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, amyl methacrylate and hexyl methacrylate. Preferably the polymers contain at least 50% by weight of said methacrylic acid ester. 100

Examples of monomers which can be copolymerized with the monomers represented by Formula I, or which can be polymerized either singly or in a plurality (two, three, four or any desired number) are such monomers as the unsaturated alcohol esters, more particularly the allyl, methallyl, crotyl, 1-chloro-allyl, 2-chloro-allyl, vinyl, methvinyl, 1-phenylallyl and butenyl esters of saturated and unsaturated aliphatic and aromatic monobasic and polybasic acids such, for instance, as acetic, propionic, butyric, valeric, caproic, crotonic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, maleic, fumaric, citraconic, mesaconic, itaconic, benzoic, phenylacetic, phthalic, terephthalic and benzoylphthalic, acids; the saturated monohydric 120 alcohol esters, e.g., the methyl, ethyl, propyl, isopropyl, butyl, sec.-butyl and amyl, esters of

ethylenically unsaturated aliphatic monobasic and polybasic acids, illustrative examples of which appear above; vinyl cyclic compounds (including monovinyl aromatic hydrocarbons),
 5 e.g., styrene, o-, m-, and p-chlorostyrenes, -bromostyrenes, -fluorostyrenes, -methylstyrenes, -ethylstyrenes, -cyanostyrenes, the various poly-substituted styrenes such, for example, as the various di-, tri-, and tetra-
 10 chlorostyrenes, -bromostyrenes, -fluorostyrenes, -methylstyrenes, -ethylstyrenes and -cyanostyrenes, vinyl naphthalene, divinyl benzene, trivinyl benzene, allyl benzene, diallyl benzene, the various allyl cyanostyrenes, the various alpha-substituted styrenes and
 15 alpha-substituted ring-substituted styrenes, e.g., alpha-methyl styrene and alpha-methyl-paramethyl styrene; unsaturated ethers, e.g., ethyl vinyl ether, diallyl ether; unsaturated amides, for instance, acrylamide and N-substituted
 20 acrylamides, e.g.; N-methylol acrylamide, N-allyl acrylamide, N-methyl acrylamide, N-phenyl acrylamide; unsaturated ketones, e.g., methyl vinyl ketone, methyl allyl ketone; ethylene; unsaturated polyhydric alcohol (e.g.,
 25 butenediol) esters of saturated and unsaturated, aliphatic and aromatic, monobasic and polybasic acids.

Other examples of monomers that can be polymerized alone or with the monomers of
 30 Formula I are the vinyl halides, more particularly vinyl chloride, vinyl bromide and vinyl iodide, and the various vinylidene compounds, including the vinylidene halides, e.g.,
 35 vinylidene chloride, vinylidene bromide, vinylidene fluoride and vinylidene iodide.

Among the comonomers which are preferred for use in carrying our invention into effect by copolymerizing them with the monomers of
 40 Formula (I) are, for example, compounds such as acrylonitrile, the various substituted acrylonitriles (e.g. methacrylonitrile, ethacrylonitrile, phenylacrylonitrile) the various N-substituted
 45 acrylamides and alkacrylamides, for instance, N-dialkyl acrylamides and methacrylamides, e.g. N-dimethyl, -diethyl, -dipropyl, -dibutyl, acrylamides and methacrylamides, styrene.

Of course, it is also possible to utilize copolymers produced from two or more of the
 50 monomers represented by Formula I, above, and still obtain the benefits heretofore set forth.

In regard to the grafting of the rubber, any monomer or group of monomers set forth
 55 above in reference to component (1) may be used. Again the compounds of Formula I are preferred. The weight ratio of rubber to grafted monomer may range from 5:1 to 0.5:1, and preferably from 3:1 to 1:1, respectively.

Once the two components of our novel composition are produced, with refractive
 60 indices matched within 0.009, they are then physically blended together to form our novel molding compositions, in any known manner,

such as for example, utilizing a ball mill, hot rolls or emulsion blending employing from 5 to 50 parts, by weight, of the grafted rubbery compounds and from 50 to 95 parts, by weight, of the polymeric component.

It is preferred, however, that the blending operation be carried out by preparing a stream
 70 of each of the components, i.e. a polymer solution and a rubbery latex, in a form enabling accurate metering of these components in proportions to produce the desired composition, to a devolatilizer-extruder where the two streams are mixed, compounded, devolatilized and extruded in a very short period
 75 of time. In the devolatilizer-extruder, the mixture is worked in a chamber under heat and vacuum so that new surfaces of the polymer mixture are continuously and rapidly exposed to vacuum to remove the monomeric solvent (and water where rubber in latex form is
 80 used) before extruding the product. The term "devolatilization" as herein employed refers to the step in which the non-polymeric material is removed from the mixture of polymer solution and rubbery latex or dispersion. The
 85 apparatus which simultaneously devolatilizes and extrudes the material is of a commercially available design and comprises a chamber with one or more screws having a close tolerance with the wall for compounding the material
 90 in its passage therethrough, and at least one vacuum chamber for removing the volatile components of the feed. The action of working the material under the close tolerance of the screws not only intimately blends the mixture, but generates substantial heat which aids
 95 in the devolatilizing of the blend.

The devolatilizer-extruder may contain one or more interconnected sections, at least one
 100 being under vacuum. A preferred treatment wherein the material is worked for a total time of from about 1 to 5 minutes, employs two vacuum sections. In addition to the vacuum sections, the devolatilizer-extruder may contain
 105 a section following the vacuum sections which is atmospheric, i.e. not under vacuum, wherein various volatiles or non-volatile modifiers, plasticizers, or colorants, may be incorporated into the composition and extruded therewith.

The vacuum sections of the devolatilizer-extruder are heated to temperatures of from
 110 110°C. to 245°C. and maintained under vacuum at an absolute pressure of from 5 mm. to 200 mm. mercury. Preferably, the temperature of the sectionally heated apparatus is maintained at from 160°C. to 210°C. and the vacuum is preferably maintained at from 5 mm. to 90 mm. mercury absolute pressure. As the two streams are introduced into the
 115 devolatilizer-extruder the increased temperature causes volatilization of the nonpolymer therefrom. At the same time, because the extruder is maintained at subatmospheric pressures, the volatile material is withdrawn or volatilized from the polymer-containing material. It
 120 125 130

should be noted that the present process does not concern the polymerization of the two components of our novel composition in the blending step, but the blending in the devolatilizer-extruder rather concerns the blending in combination with the removal of the volatile ingredients from the two components. In fact, the rapid passage of the components through the devolatilizer-extruder is not conducive to any significant polymerization because of the rapidity of the step.

The stream of each component charged to the devolatilizer-extruder may be in the form of a dispersion, a solution, an emulsion of the latex, with any known solvent for the polymer and the grafted rubber being employed. Such compounds as benzene, toluene, xylene, aliphatic esters, naphthalene, tetralin, trichlorobenzene, and dimethylformamide are exemplary and, as such, may be used in our process.

Preferably, however, the monomeric compound from which the major proportion of hard resinous polymer is derived is employed as the solvent for both the polymer component and the grafted rubber component when the rubber is blended in solution rather than as a latex.

In the devolatilizer-extruder, the volatile ingredients of the components are thoroughly removed as the mixture is worked, by the heat generated by the mechanical action of the devolatilizer screw under vacuum. By this technique, the rate of diffusion is so improved that substantially 100% of the undesirable volatiles are removed, thereby producing a molding composition having high impact strength and practically, free of all contaminants.

The following examples are set forth for purposes of illustration only. All parts and

percentages are by weight unless otherwise indicated.

EXAMPLE 1

(Preparation of Grafted Rubber)

A mixture of 390 parts of water, 763 parts of a 50% emulsion of polybutadiene in water, 90 parts methyl methacrylate, 293 parts styrene, 68 parts of acrylonitrile, 2.25 parts cumene hydroperoxide and an emulsifier is added to a vessel, purged with nitrogen for 7 hours and agitated at room temperature for 10 minutes. A solution of 3.15 parts of dihydroxy acetone in 200 parts of water is added, and the mixture is stirred for 5 minutes. The mixture is then left standing for 12 hours whereupon almost all the monomers have reacted. The product is an emulsion with 50% solids content. The refractive index of a clear film made from this emulsion is (D-line) 1.532.

EXAMPLE 2

(Preparation of Polymer)

The amount of monomers necessary to produce a polymer having a refractive index within 0.009 of the grafted rubber of Example 1 is calculated, for example, in the case of the three monomers, methyl methacrylate, styrene and acrylonitrile, as follows, utilizing the equation

$$n = \frac{\sum_{i=1}^K (N_i M_i n_i)}{\sum_{i=1}^K (N_i M_i)}$$

Let A equal N_i for methylmethacrylate, B equal N_i for styrene and C equal N_i for acrylonitrile.

$$1.532 = \frac{(A \times 100 \times 1.491) + (B \times 104 \times 1.591) + (C \times 53 \times 1.515)}{(A \times 100) + (B \times 104) + (C \times 53)}$$

Then on choosing a suitable value for either A, B, or C, say

A = 0.400 moles methyl methacrylate, the values of B and C can be obtained, and from the above equation are:

B = 0.311 moles styrene

C = 0.289 moles acrylonitrile

Utilizing these figures, in parts by weight, into a stainless steel reactor is charged 329 parts of methyl methacrylate, 266 parts of styrene, 105 parts of acrylonitrile, 300 parts of toluene, 2.0 parts of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, and 1.4 parts of lauryl mercaptan. The mixture is stirred and kept at 100°C. for 26 hours, whereupon almost all the monomers react. The solution is milled at 170°C. until all the toluene and residual monomers have evaporated. The product is clear and has a refractive index of 1.532.

EXAMPLE 3

(Blending of Grafted Rubber and Polymer)

The emulsion from Example 1 and the polymer from Example 2 are masticated for 5 minutes at 170°C., all water and solvent having been volatilized. The product is granulated and yields a clear impact material when injection molded. The Izod impact strength of the material is 3.7 fppi. The material contains 80% of the polymer of Example 2.

EXAMPLE 4

(Preparation of Grafted Rubber)

A mixture of 390 parts of water, 750 parts of an emulsion of a styrene-butadiene copolymer containing 29% styrene, 360 parts of methyl methacrylate, 23 parts of styrene, 68 parts of acrylonitrile, 2.25 parts of cumene hydroperoxide, and an emulsifier is added to a suitable reaction vessel, purged with nitrogen

for 1 hour and agitated at room temperature for 10 minutes. A solution of 3.15 parts of dihydroxy acetone in 200 parts of water is added and the mixture polymerized as described in Example 1. The refractive index of a clear film made from the emulsion at 25°C. is 1.522.

EXAMPLE 5

(Preparation of Polymer)

A mixture of 413 parts of methyl methacrylate, 182 parts of styrene, and 105 parts of acrylonitrile is polymerized in 300 parts of toluene with 2.0 parts of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane and 1.4 parts of lauryl mercaptan as a modifier, the determination of the amounts of monomer to be used and the polymerization being carried out as described in Example 2. The clear product has a refractive index of 1.521.

EXAMPLE 6

(Blending Grafted Rubber with Polymer)

The emulsion from Example 4 and the polymer from Example 5 are masticated for 5 minutes on a roll mill at 170°C. The product is granulated and injection molded. The Izod impact strength of the clear product is 3.1 fppi. The material contains 80% of the polymer of Example 5.

EXAMPLE 7

(Preparation of Grafted Rubber)

A mixture of 390 parts of water, 763 parts of an emulsion of polybutadiene, 315 parts of methyl methacrylate, 135 parts of acrylonitrile, 2.25 parts of cumene hydroperoxide, and a emulsifier is purged with nitrogen and agitated as described in Example 1. A solution of 3.15 parts of dihydroxyacetone in 200 parts of water is added and the polymerization is then carried out as in Example 1. The refractive index of clear film made from the emulsion is 1.509.

EXAMPLE 8

(Preparation of Polymer)

Into a vessel is charged, under stirring,

Izod notched impact strength	— 4.6 fppi.
Deflection temperature under load	— 79°C.
Rockwell Hardness (Scale R)	— 99
Tensile Strength	— 5,200 psi
Tensile modulus	— 0.29 10 ⁶ psi
Tensile elongation at yield	— 3.7%

EXAMPLE 13

(Preparation of Grafted Rubber)

A mixture of 362 parts of water, 763 parts of an emulsion of polybutadiene in water, 142 parts of methyl methacrylate, 38.0 parts of styrene, and 45.0 parts of acrylonitrile is heated as described in Example 1. The ensuing emulsion gives a clear film with a refractive index of 1.515.

1700 parts of water and 40.0 parts of sodium lauryl sulfate. The solution is heated to 60°C. and a mixture of 700 parts of methyl methacrylate, 300 parts of acrylonitrile and 5 parts of dodecyl mercaptan is added dropwise, simultaneously with a solution of 5.0 parts of ammonium persulfate in 300 parts of water. The calculation procedure of Example 2 is again followed. After the monomers are converted to polymers, the refractive index of a film cast from the emulsion is 1.500.

EXAMPLE 9

(Blending of Grafted Rubber and Polymer)

The grafted latex from Example 7 and the polymer emulsion from Example 8 are mixed together in such proportions that the polybutadiene content of the solids is 20%. The emulsion is coagulated, washed, dried and densified in an extruder. Injection molding gives clear transparent hues with an Izod impact strength of 7.2 fppi.

EXAMPLE 10

(Preparation of Grafted Rubber)

A mixture of 297 parts of methyl methacrylate, 85.5 parts of styrene, and 67.5 parts of acrylonitrile is polymerized with 763 parts of a polybutadiene latex as described in Example 1. A film cast from the emulsion has a refractive index 1.516.

EXAMPLE 11

(Preparation of Polymer)

A mixture of 660 parts of methyl methacrylate, 190 parts of styrene, and 150 parts of acrylonitrile are emulsified and polymerized as described in Example 8. The ensuing polymer emulsion has a refractive index of 1.515.

EXAMPLE 12

The emulsions from Examples 10 and 11 are mixed so that the polybutadiene content of the solids is 20%, and the emulsion is coagulated, washed, dried, and extruded. The compound is injection molded into transparent bars having the following physical properties:

EXAMPLE 14

(Preparation of Polymer)

A mixture of 36.75 parts of methyl methacrylate, 9.8 parts of styrene, and 2.45 parts of acrylonitrile is polymerized in 21.0 parts of xylene with 0.15 part of 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane using 0.05 part of n-dodecyl mercaptan as a regulator. After evaporating the solvent and small amounts of

residual monomers on a roll mill, the refractive index of the product is 1.518.

EXAMPLE 15

(Blend of Polymer and Grafted Rubber)

5 The polymer from Example 14 and the latex from Example 13 are mixed on a roll mill in such proportions that the solids contain 20% polybutadiene. The molded product is clear and transparent and has an Izod impact strength of 3.5 fppi, and a deflection temperature under load of 90°C.

EXAMPLE 16

15 An emulsion of a styrene-butadiene copolymer containing 29% styrene is mixed with equal proportions, based on the weight percent of solids in the emulsion, of a mixture of methyl methacrylate, styrene and acrylonitrile monomers in weight proportions of 48/47/5. Initiator and emulsifier are added as described in Example 1 and the mixture is polymerized to 98.5% conversion of the monomers. Simultaneously a terpolymer of methyl methacrylate, styrene and acrylonitrile in weight proportions of 50/45/5 is prepared as described in Example 2. The emulsion containing the resultant grafted rubber has a refractive index of 1.539 and the terpolymer has a refractive index of 1.542. The two components are mixed on a hot roll mill in such proportions that the final product contains 20% by weight of rubber, calculated as styrene-butadiene copolymer. The clear transparent product has an Izod impact strength (notched) of 2.4 fppi, and a distortion temperature under load of 85°C.

EXAMPLE 17

35 An emulsion of polyisoprene is mixed with equal proportions, based on the weight percent of the solids in the emulsion, of a mixture of methyl methacrylate, styrene, and acrylonitrile monomers in a weight ratio of 55/35/10. Initiator and emulsifier are added as described in Example 1, and the mixture is polymerized to 95% conversion of the monomers. The graft copolymer thus obtained has a refractive index of 1.524. Simultaneously, a terpolymer of methyl methacrylate, styrene and acrylonitrile in weight proportions of 60/30/10 is prepared as described in Example 2. The terpolymer has a refractive index of 1.526. The emulsion of the graft copolymer and the terpolymer solution are blended on a hot mill roll, so that the final product contains 25% polyisoprene, by weight. The clear transparent product has an Izod impact strength of 1.9 fppi and a heat distortion temperature under load of 79°C.

EXAMPLE 18

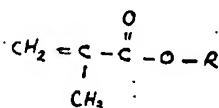
60 An emulsion of an acrylonitrile-butadiene copolymer, containing 30% acrylonitrile, is mixed with equal proportions, based on the weight percent of solids in the emulsion, of

a mixture of methyl methacrylate, styrene and acrylonitrile monomers in weight proportions of 45/50/5. Initiator and emulsifier are added as described in Example 1 and the mixture 65 graft polymerized to 98% conversion. The ensuing grafted copolymer has a refractive index of 1.528. Simultaneously a terpolymer of methyl methacrylate, styrene and acrylonitrile in weight proportions of 60/35/5 is 70 prepared as described in Example 2. The terpolymer has a refractive index of 1.533. The emulsion containing the grafted copolymer and the terpolymer are mixed on a hot roll mill in such proportions that the final product contains 20% by weight rubber, calculated as acrylonitrile-butadiene copolymer. The clear transparent product has an Izod impact strength of 2.6 fppi and a distortion temperature under load of 83°C. 80

WHAT WE CLAIM IS:—

1. A transparent thermoplastic molding composition comprising a physical admixture of (1) from 50 to 95 parts by weight of a polymer composed of at least one polymerizable monomer containing ethylenic unsaturation and (2) from 5 to 50 parts by weight of a natural or a synthetic rubber, said rubber having grafted thereon a polymer composed of at least one monomer possessing ethylenic unsaturation, the refractive indices of said components (1) and (2) being within 0.009 of one another, both components (1) and (2) being transparent. 85 90

2. A transparent thermoplastic molding composition comprising a physical admixture of (1) from 50 to 95 parts by weight of a polymer of a methacrylic acid ester monomer having the formula 95



wherein R represents an alkyl radical having from 1 to 6 carbon atoms, inclusive, said polymer containing at least 50% by weight of said methacrylic acid ester, the remaining monomer, if any, being an ethylenically unsaturated monomer copolymerizable therewith and (2) from 5 to 50 parts by weight of a natural or a synthetic rubber, said rubber having grafted therein a polymer composed of at least one monomer possessing ethylenic unsaturation, the refractive indices of said components (1) and (2) being 0.009 of one another, both components (1) and (2) being transparent. 100 105 110

3. A composition according to Claim 2 wherein the methacrylic acid ester is methyl methacrylate and the rubber is polybutadiene. 115

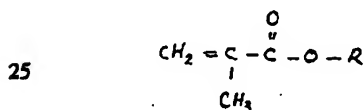
4. A method of producing a transparent thermoplastic molding composition which comprises (1) polymerizing at least one polymeriz- 120

able monomer containing ethylenic unsaturation such that the polymer produced is transparent and has a refractive index within 0.009 of a transparent grafted natural or synthetic rubber with which the polymer is to be blended, the molar amounts of monomer employed being calculated from the equation:

$$n = \frac{\sum_{i=1}^K (N_i M_i \eta_i)}{\sum_{i=1}^K (N_i M_i)}$$

wherein N_i is the mole fraction of monomer i , M_i is the molecular weight of monomer i , η_i is the refractive index of the homopolymer of the monomer i , wherein i runs from 1 to K and wherein K is the number of monomers involved in the polymerization, and η is the refractive index of the grafted rubber and (2) physically blending from 50 to 95 parts by weight of the polymer produced in step (1) with from 5 to 50 parts by weight of said grafted rubber.

5. A method of producing a transparent thermoplastic molding composition which comprises polymerizing at least 50% by weight of a methacrylic acid ester having the formula



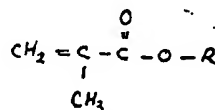
wherein R is an alkyl radical having 1 to 6 carbon atoms, inclusive, the remaining monomer, if any, being an ethylenically unsaturated monomer copolymerizable therewith, such that the resultant polymer is transparent and has a refractive index within 0.009 of a transparent grafted natural or synthetic rubber with which the polymer is to be blended, the molar amounts of said monomers employed being calculated from the equation.

$$n = \frac{\sum_{i=1}^K (N_i M_i \eta_i)}{\sum_{i=1}^K (N_i M_i)}$$

wherein N_i is the mole fraction of monomer i , M_i is the molecular weight of monomer i , η_i is the refractive index of the homopolymer of the monomer i , wherein i runs from 1 to K and wherein K is the number of monomers involved in the polymerization, and η is the refractive index of the grafted rubber, and (2) physically blending from 50 to 95 parts by weight of the polymer produced in step (1) with from 5 to 50 parts by weight of said grafted rubber.

6. A method of producing a transparent thermoplastic molding composition which comprises (1) graft polymerizing a natural or synthetic rubber with at least one ethylenically unsaturated monomer, the amount of monomer grafted being such that the resultant grafted rubber is transparent and has a refractive index within 0.009 of that of the transparent polymer, composed of at least one monomer containing ethylenic unsaturation, with which the grafted rubber is to be blended and (2) physically blending 5 to 50 parts, by weight, of the grafted rubber produced in step (1) with 50 to 95 parts, by weight, of the transparent polymer.

7. A method of producing a transparent thermoplastic molding composition which comprises (1) graft polymerizing a natural or synthetic rubber with at least one ethylenically unsaturated monomer, the amount of monomer grafted being such that the resultant grafted rubber is transparent and has a refractive index, within 0.009 of that of a transparent polymer with which the grafted polymer is to be blended and which is derived, wholly or in part of a monomer having the formula



wherein R represents an alkyl radical having from 1 to 6 carbon atoms, inclusive, said polymer containing at least 50% by weight of said monomer, the remaining monomer, if any, being an ethylenically unsaturated monomer copolymerizable therewith, and (2) physically blending 5 to 50 parts, by weight, of the grafted rubber produced in step (1) with 50 to 95 parts, by weight, of the transparent polymer.

8. A method according to claim 4 or claim 6 of producing a transparent thermoplastic

molding composition substantially as described.

9. A transparent thermoplastic molding composition whenever prepared by the method according to claim 8.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

